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Version of attached file:

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Peer-review status of attached file:

Peer-reviewed

Citation for published item:

TorresZiegenbein, Christian and Fröbel, Sascha and Glöß, Maria and Nobuyasu, Roberto S. and Data, Przemyslaw and Monkman, Andrew and Gilch, Peter (2017) 'Triplet harvesting with a simple aromatic carbonyl.', *ChemPhysChem.*, 18 (17). pp. 2314-2317.

Further information on publisher's website:

<https://doi.org/10.1002/cphc.201700683>

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CHEMPHYSCHEM

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Accepted Article

Title: Triplet Harvesting with a Simple Aromatic Carbonyl

Authors: Christian Torres Ziegenbein, Sascha Fröbel, Maria Glöß,
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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: *ChemPhysChem* 10.1002/cphc.201700683

Link to VoR: <http://dx.doi.org/10.1002/cphc.201700683>

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Triplet Harvesting with a Simple Aromatic Carbonyl

Christian Torres Ziegenbein, Sascha Fröbel, Maria Glöß, Roberto S. Nobuyasu, Przemyslaw Data, Andrew Monkman, and Peter Gilch*

Abstract: The efficiency of organic light emitting diodes crucially depends on triplet harvesters. These accept energy from triplet correlated electron hole pairs and convert it into light. Here experimental evidence is given that simple aromatic carbonyls, such as thioxanthone, could serve this purpose. In these compounds the emissive $^1\pi\pi^*$ excitation may rapidly equilibrate with an upper triplet state ($^3n\pi^*$). This equilibrium may persist for nanoseconds. Population of the $^3n\pi^*$ state via energy transfer from an electron hole pair should result in fluorescence emission and thereby triplet harvesting. To demonstrate the effect, solutions 1,4-dichlorobenzene (triplet sensitizer) and thioxanthone (harvester) were excited at 266 nm with a nanosecond laser. The emission decay reveals a 100 ns decay absent in the thioxanthone only sample. This matches predictions for an energy transfer limited by diffusion and gives clear evidence that thioxanthone can convert triplet excitations into light.

Organic light emitting diodes (OLEDs) gain more and more importance in display^[1] and illumination technology^[2]. Therefore, OLEDs with a high plug efficiency are very desirable. One issue in this context is related with spin statistics. In the emission layer of an OLED, injected holes and electrons recombine radiatively (for a recent review see ref. [3]). Electrons and holes are spin 1/2 (quasi) particles. Because of the statistical nature of the charge recombination process they form triplet and singlet pairs. Of all pairs, 3/4 have triplet multiplicity. On their own, these pairs cannot recombine radiatively. This severely limits the internal quantum efficiency of OLEDs and has triggered huge efforts to mitigate it^[3-4] (Figure 1).

To this end, OLEDs are doped with emitters in which the pairs recombine. To harvest the energy of the triplet pairs, these emitters either exhibit efficient phosphorescence (I^[4b, 5]) or allow for triplet to singlet transitions followed by fluorescence (II^[6] and III^[7]). In approach I^[4b, 5], transition metal ions in suitable organic ligand complexes remove the spin forbiddance of the radiative transition by virtue of their large spin-orbit coupling

(SOC)^[8]. Presently, costly iridium and platinum complexes are employed^[9], but copper complexes have been considered as well^[10]. In approach II^[6], organic charge transfer molecules may be employed. In these systems, the excitation lowest in energy is a triplet state with charge transfer (CT) character. Because of this character the exchange interaction ΔE separating singlet and triplet CT states is small, of the order of the thermal energy $k_B T$. This can allow for the population of the singlet CT state followed by fluorescence emission.

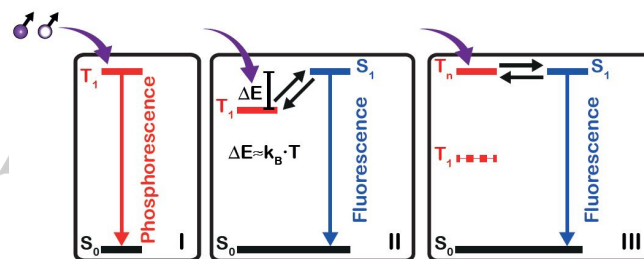


Figure 1. Different approaches for triplet harvesting in OLEDs discussed in the text.

Another requirement is that the rate constant of reverse intersystem crossing (rISC) has to be larger than the rate constant for the depletion of the triplet CT state. rISC is mediated by SOC. Direct SOC between singlet and triplet CT states are commonly negligible^[11]. However, vibronic couplings can mix the triplet CT state with local triplet excitation and thus enhance SOC^[11]. This may result in efficient rISC and hence in thermally activated delayed fluorescence (TADF)^[11-12].

One problem with this approach is that a small exchange interaction often also gives rise to small radiative rate constants of the fluorescence^[13]. This renders non-radiative processes competitive and can reduce the luminescence efficiency. In approach III^[7] one tries to avoid this by relying on upper excited triplet states T_n . Here, an upper triplet state needs to be in energetic vicinity with or above a singlet excited state (notionally S_1) which should feature a large radiative rate constant. Further, internal conversion (IC) between triplet states (rate constant $k_{IC,T}$ cf. Figure 2) needs to be slow compared to the upper rISC (rate constant k_{rISC})^[7].

Here, we give first evidence that in a surprisingly simple class of molecules, namely aromatic carbonyls, this process is active (Figure 2). Prior femtosecond experiments performed by the Gilch group^[14] and quantum chemical computations of the Marian group^[15] revealed a peculiar behavior of xanthone (X) and thioxanthone (TX). In protic solvents, their bright S_1 states ($^1\pi\pi^*$ character) accessed by optical excitation equilibrate with their T_2 states ($^3n\pi^*$ character). The two states are nearly iso-energetic. The equilibration is established within 1-10 ps implying that ISC and hence rISC occur on that time scale. Surprisingly, the equilibrium persists for nanoseconds, i.e. $k_{IC,T} \ll k_{ISC} + k_{rISC}$. The results suggest that the two states are strongly coupled and we will show here that population of the T_2 state results in fluorescence emission (from S_1). Thus, the compounds can act as triplet energy harvesters. To demonstrate this we

[*] C. Torres Ziegenbein, Dr. S. Fröbel, M. Glöß, and Prof. P. Gilch
Institut für Physikalische Chemie
Heinrich-Heine-Universität Düsseldorf
Universitätsstr. 1, D-40225 Düsseldorf (Germany)
E-mail: gilch@hhu.de
Dr. S. Fröbel
Current address: Department of Chemistry
The Ohio State University
100 West 18th Avenue, Columbus, OH 43210 (USA)
R. S. Nobuyasu, Dr. P. Data, Prof. A. Monkman
Department of Physics
Durham University
Durham DH1 3LE (United Kingdom)
Dr. P. Data
Faculty of Chemistry
Silesian University of Technology
M. Strzody 9, 44-100 Gliwice (Poland)

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access their T_2 state via a molecular sensitizer. The sensitizer acts as a “stand-in” for triplet pairs generated electrically in an OLED^[16].

Since TX in methanol is the system most thoroughly characterized by us^[14b, 14c, 15b] we have selected a sensitizer for it.

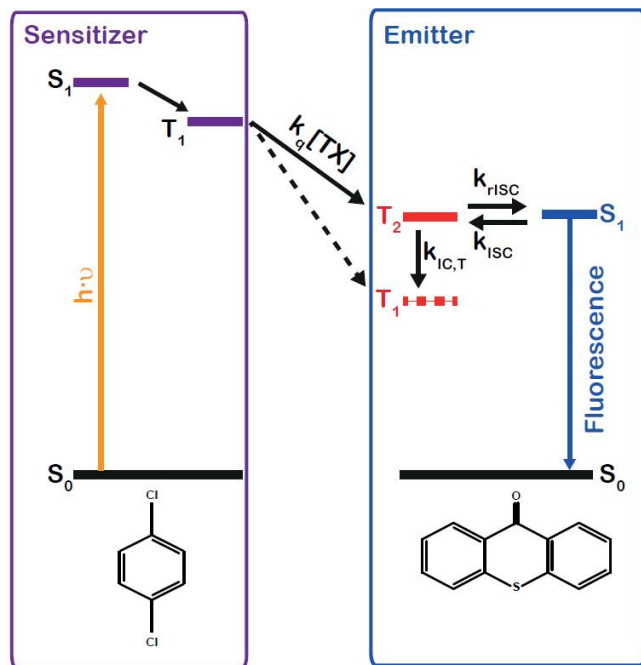


Figure 2. Kinetic scheme of the sensitization experiment described here.

By inspecting properties listed in the “Handbook of Photochemistry”^[17] 1,4-dichlorobenzene (DCB) was identified as a suitable sensitizer. The adiabatic energy of its T_1 state is 3.47 eV^[18] and, thus, exceeds the T_2 energy of TX in methanol of 3.2 eV^[14c, 15b]. Its triplet yield Φ_T^s is close to unity^[19]. Its absorption spectrum is compared with that of TX in Figure 3. From the spectra it may be inferred that an exclusive excitation of the sensitizer is not possible. This also applies to other potential sensitizers.

Steady state spectroscopy gives a first indication for triplet harvesting by TX. Argon purged solutions of TX in methanol (0.1 mM) and varying concentrations of DCB (2–4 mM) were excited at 280 nm. The fluorescence signal of TX peaking at 430 nm decreases with increasing DCB concentration (not shown). This decrease is due to the primary inner filter effect^[20]. In spectra corrected for this effect (Figure 3, correction is described in the SI, Figures S1 and S2) an increase of the emission with growing DCB concentration is observed. This increase indicates an energy transfer from DCB to TX, which then results in increased fluorescence emission from TX.

The time resolved fluorescence spectroscopy described now gives proof that this increase involves the upper triplet state of TX and is *not* related to singlet energy transfer, e.g. via the Förster mechanism^[21]. Nitrogen purged solutions were excited with nanosecond laser pulses centered at 266 nm. Fluorescence emission was measured using a spectrograph coupled to a gated ICCD camera^[22]. The spectrally integrated fluorescence trace of the TX only solution (1.1 mM) features a decay in the

nanosecond range due to the direct excitation of TX (Figure 4). The behavior is in line with the reported fluorescence lifetime of TX in methanol (~2.5 ns^[14c]). A second component decays on the time scale of 10 ns. Due to its spectral characteristics and concentration dependence (not shown) it can be attributed to an excimer.

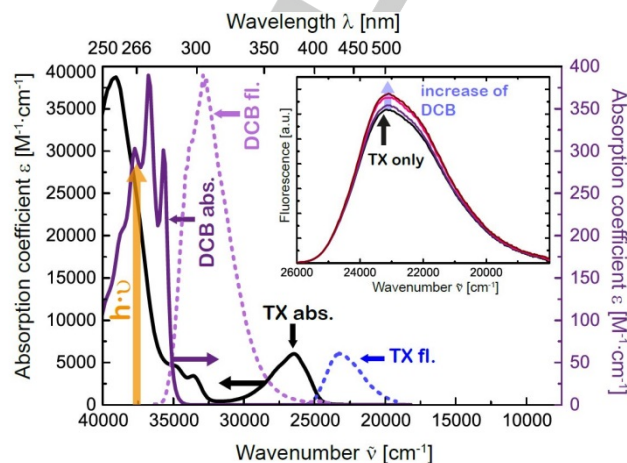


Figure 3. Steady state absorption and fluorescence spectra (excitation 280 nm) of the sensitizer DCB and the emitter TX dissolved in methanol. The right ordinate gives the absorption coefficients of DCB, the left one those of TX. Note that the fluorescence spectra were scaled to match the height of the respective absorption band. They are not proportional to quantum yields. The insert shows the increase of the TX fluorescence corrected for inner filter effects upon addition of DCB. The yellow arrow marks the excitation wavelength (266 nm) for the time resolved experiment.

A component with a time constant of ~ 3 μs is ascribed to triplet-triplet annihilation (TTA). Such a TTA process has already been reported for TX in methanol^[14b]. Addition of DCB (0.1 M) reduces the amplitude of the initial component due to the inner filter effect. Most importantly, a component absent in TX only and DCB only solutions appears. Its spectrum is identical to the fluorescence emission of TX. An exponential fit of this component yields a time constant τ_{EET} of 100 ns. Of the kinetic processes summarized in Figure 2 the intermolecular energy transfer from the DCB sensitizer to the TX ought to be rate determining. Its time constant τ_{EET} should obey the relation $\tau_{EET} = 1 / (k_q [TX])$. An estimate assuming diffusion controlled quenching, i.e. the quenching constant $k_q = k_{diff} = 1.1 \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for processes in methanol^[17], and inserting the concentration $[TX] = 1.1 \text{ mM}$ yields $1 / (k_q [TX]) = 82 \text{ ns}$. This is very close to the experimental value. A reduction of the concentration $[TX]$ to 0.55 mM results in the predicted rise of the time constant τ_{EET} to 210 ns (see Figure 4). The measured time constants τ_{EET} are much longer than the singlet lifetime of DCB of < 1 ns (see SI, Figure S3). Thus, the energy transfer has to involve the triplet state of DCB.

As can be seen in Figure 2, the triplet energy transfer may populate two final states (T_1 and T_2). To determine the fraction of energy transfers that lead to the population of the *upper* triplet state, which then gives rise to the increased emission, an efficiency η_{em} can be calculated. It is estimated from the fluorescence decay traces. To this end, two temporal integrals

were computed (see Figure 4). The first I_{dir} covers the decay due to direct excitation of TX. The second, I_{sens} , due to sensitized excitation. The integral I_{dir} was divided by the fraction of light absorbed by TX, the second integral, I_{sens} , by the one absorbed by the sensitizer DCB. The efficiency is finally given by the ratio of these normalized integrals, $\eta_{em} = I_{sens}^N / I_{dir}^N$. For the 1.1 mM TX data set depicted in Figure 4 we calculate an efficiency η_{em} of ~ 0.01 – 0.02 . The range given accounts for the fact that the lower boundary of the integral I_{sens} is not well defined because of TTA. A determination based on the steady state spectra given in Figure 3 yields a value of similar magnitude (~ 0.06 , see SI, Figure S2).

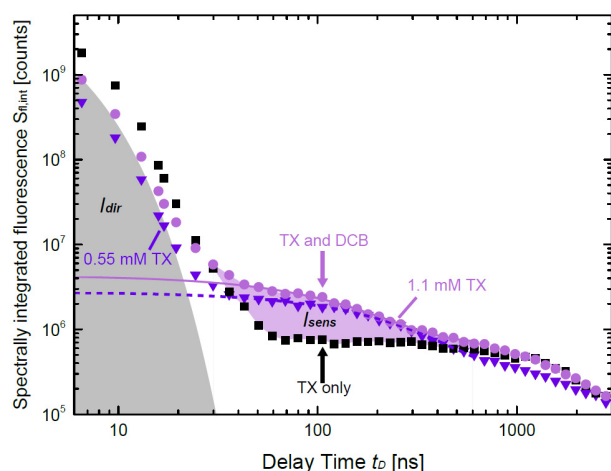


Figure 4. Spectrally integrated fluorescence decay traces of TX in methanol in absence (black) and presence of DCB (violet). Symbols represent experimental data. The lines stand for single exponential fits of the additional component due to sensitization by DCB. Integrals used to compute the efficiency η_{em} are marked. Note that the integral I_{dir} extends to smaller delay times not included in the diagram. Its value was obtained by fitting the initial decay with an exponential convoluted with the instrumental response function. The time constant of the exponential was equal to the fluorescence lifetime of TX.

The time constants τ_{EET} are much smaller than the triplet lifetime of DCB^[19b], which indicates that the DCB triplet states are quenched with a yield close to 100%. Hence, the low efficiency η_{em} for the population of the upper triplet state of TX implies that the transfers result to a smaller degree in the population of the upper triplet state T_2 and to a larger part to that of the lower triplet state T_1 (dashed arrow in Figure 2). Nanosecond transient absorption experiments also give evidence for this kind of branching (see SI, Figure S4). Because of the large energy gap between the bright S_1 and the T_1 state^[14c] only the population ending up in the T_2 state contributes to enhanced S_1 emission.

The experimental results presented here give evidence that due to their upper triplet states, having $^3n\pi^*$ character, some simple aromatic carbonyl compounds might serve as triplet harvesters in OLEDs. The compound TX, which is studied here because of the wealth of photo-physical data available, is not ideal for this purpose. In any solvent, its fluorescence quantum yield is below 0.5 ^[23]. However, related compounds such as

acridone derivatives feature yields close to unity^[24]. These high yields have been attributed to the T_2 state lying above the S_1 state, greatly reducing ISC^[24–25]. This would in turn shift the rISC equilibrium towards the S_1 state. The equilibration is expected to remain fast^[25]. This should ensure that once the T_2 state is populated (by charge recombination) all energy is released radiatively. More critical is the question whether the unproductive population of the lowest triplet state T_1 observed here for a molecular sensitizer can be avoided in an actual device. Recent findings by Hu et al.^[7a] that upper triplet states can be relied on in OLED devices are very promising in this context.

Acknowledgements

We are grateful to our former bachelor student Florian Hyseni for experimental support. S.F. acknowledges funding by the Alexander von Humboldt-Foundation (Feodor Lynen Research Fellowship). P.D. thanks the EU for a Marie Curie Fellowship H2020 research and innovation programme under grant agreement No 659288. R.S.N. thanks to networking action funded from the European Union's Horizon 2020 research and innovation programme under grant agreement No 691684. R.S.N. also thanks CAPES Foundation, Ministry of Education of Brazil, Science Without Borders Program for a PhD studentship, Grant No. BEX9474-13-7.

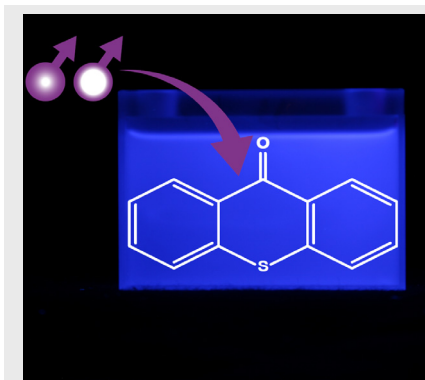
Keywords: aromatic carbonyls • fluorescence • time-resolved spectroscopy • OLED • triplet emitter

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COMMUNICATION

Aromatic carbonyls such as thioxanthone are shown to be potential triplet harvesters for organic light emitting diodes.



Christian Torres Ziegenbein, Sascha Fröbel, Maria Glöß, Roberto S. Nobuyasu, Przemysław Dąta, Andrew Monkman, Peter Gilch*

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